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MINISTRY OF AVIATION

EXPLOSIVES RESEARCH & DEVELOPMENT ESTABLISHMENT

TECHNICAL MEMORANDUM No. 6/M/60

An Investigation of the Explosive Hazards of Ammonium Perchlorate/Polyurethane Rubber Propellants in the Uncured and Cured Conditions

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by

J.K. Clark and P.D. Verschoyle

(Sept 1960)

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CONTENTS

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1. SUMMARY

Trials have been carried out to determine what precautions and safety distances would be appropriate to the risks involved in the mixing, curing and storage of two polyurethane/ammonium perchlorate propellants.

Uncured propellant was tested in three types of vessel,

(a) 3 inches I.D. with ⅜ inch wall, containing 1700 g. of propellant.

(b) 12 inches I.D. with 9/32 inch wall thickness (calculated bursting strength 3160 p.s.i.) containing 100 lb of propellant.

(c) in two mock-up incorporators, 3 ft diameter, ⅛ inch wall thickness, each containing 1000 lb of propellant.

The propellant was ignited either by heating the containers externally or by firing a 7 g. SR 371C igniter inside the container.

Cured propellants were tested in 12-inch diameter containers by heating over fires only.

In these conditions the propellant showed no sign of detonation, and very little blast was produced. It was concluded that the propellants tested could be treated as a "Y" risk, the operatives being protected from fragments, and that for future trials, the 12-inch diameter vessel containing 100 lb of propellant could suitably be used to simulate a larger diameter, but weaker, vessel containing a greater weight of propellant.

2. INTRODUCTION

The investigation was made to determine what precautions were necessary during the mixing, filling, curing and storage of polyurethane/ammonium perchlorate propellants.

At E.R.D.E. it had been decided as standard practice, when manufacturing propellants containing aluminium, to mix the aluminium with the polyester before the ammonium perchlorate was added, since "dry" mixtures of aluminium and perchlorate were known to be dangerous. It was thought that, although this particular danger had been avoided, there might still be a dangerous phase during the mixing process, since early work (1) had shown ammonium perchlorate by itself to be capable of sustaining detonation, and it seemed probable that, when mixed with organic material in certain proportions, its sensitiveness might be increased. The early series of tests were therefore designed to simulate different stages in the mixing process, after the addition of perchlorate to the aluminium/polyester mixture.

The propellant chosen for these tests was "P2", which had the following composition:

/Ammonium .....

Ammonium perchlorate	61.5
Polyester	20.64
Tolylene di-isocyanate	1.86
Ionol	1.0
Aluminium	15

For trials intended to simulate the mixing process the tolylene di-isocyanate (T.D.I.) cross-linking agent was omitted, to ensure that the material was in the uncured condition when tested some time after mixing.

3. TEST METHODS AND RESULTS

3.1 Tests in 3-inch Diameter Thick-walled Steel Tubes

Preliminary trials were made in vessels fabricated from mild steel tubing of ⅜-inch wall thickness and 3 inches internal diameter (Fig. 1). The vessels were approximately half-filled with propellant ingredients.

In some tests the vessels were heated until a burst occurred, by means of electrical resistance windings round the outside. This heated vessel had been developed at E.R.D.E. as a possible replacement for the 5.5-inch shell for use in trials for the categorisation of propellants. Owing to difficulties with temperature recording equipment the rate of temperature rise in the present experiments was not well controlled.

In other trials in these containers the means of ignition was a 7-gram igniter of SR 371C either immersed to about half the depth of the propellant, or placed above the propellant surface. The first of these igniter positions was intended to represent an ignition which might be produced below the surface of the propellant in the mixer if the stirrer became deformed, or was obstructed by a foreign body. The second represented an ignition of dust or vapour in the space above the propellant in the mixer. In the tests using igniters the propellant was preheated to 80° to 90°C., the temperature at which mixing might be done.

The materials tested were:

1. Ammonium perchlorate alone,
2. Aluminium, polyester, Ionol mixture, with ammonium perchlorate added in the proper proportion in the thick-walled vessel but not stirred in,
3. As in 2, except that the perchlorate was mixed with the other ingredients for different lengths of time, in a Beken mixer, before transfer to the thick-walled tube.
4. As in 2 and 3, but constituents fully mixed.

Particulars of the tests and of the results obtained are given in Table 1 (p.3) The damage to these containers is shown in Figs. 2 and 3.

3.2 Tests on 100 lb of Uncured Materials in 12-inch Diameter Containers

The containers (Fig. 4) were intended to simulate, on a reduced scale, the incorporator used for mixing the propellant. In order to compensate

/TABLE 1 .....

TABLE 1

Tests in 3-inch I.D. Thick-walled Vessels

Shot No.	Material	Conditions	Method of Initiation	Remarks
1	Ammonium Perchlorate only; 815 g. = 1 litre approximately		Heating	Pressure burst after 21½ min, Rate and temperature rise uncertain, Recorder faulty
2	Aluminium + Polyester + Ionol + Ammonium Perchlorate, unmixed Total wt. 1700 g. = 1 litre approximately		"	Pressure burst after 53 min, Rate and temperature rise uncertain
3	Ammonium Perchlorate + Polyester + Aluminium - mixed for 5 min after addition of perchlorate Total wt. 1700 g.		"	Pressure burst after 59 min.
4	Ammonium Perchlorate + Polyester + Ionol + Aluminium Fully Mixed Total wt. 1700 g.		"	Pressure burst after 55½ min.
5	Ammonium Perchlorate + Polyester + Ionol + Aluminium - Mixed for 1 min after Addition of Perchlorate Total wt. 1700 g.	Propellant Temperature 90°C.	7 g. SR.371C in middle of propellant	Burst much more violent than in Trials 1 to 4
6	Ammonium Perchlorate + Polyester + Ionol + Aluminium - Fully Mixed Total wt. 1700 g.	Propellant Temperature 90°C.	"	Burst again much more violent than in Trials 1 to 4; three fragments found 1 inch or less in diameter, indicating a vigorous explosion
7	" " " "	"	7 g. SR.371C above surface of propellant	Case remained whole; hole burned in the filler plug by propellant burning as in a rocket
8	Ammonium Perchlorate + Polyester + Aluminium + Ionol Mixed for 1 min after Addition of Perchlorate Total wt. 1700 g.	Propellant Temperature 80°C	"	Propellant burned as in a rocket, the gases issuing only through the 3/16-inch tube by which the igniter wires entered
9	" " " "	Propellant Temperature Ambient (about 25°C.)	7 g. SR.371C in middle of propellant	Pressure burst, ½ lb of propellant recovered unburnt

/for .....

for the reduction in size they were made considerably heavier in construction than the full-scale incorporator, which was fitted with a burster disc of Perspex to burst at about 40 p.s.i. The weight of propellant used for each test was 100 lb, which filled the container half-full.

One set of four containers (series A) was heated over Avtag fires until a burst occurred. In the other set of four containers (series B) a 7-gram igniter of SR 371C was fired below the surface of the propellant ingredients, which had been preheated to 60°C, since in practice the propellant is mixed hot. The materials used again represented different stages in the mixing process, after the addition of the ammonium perchlorate, but this time the partial mixing was done in the field in the trial container instead of in a Beken mixer, the perchlorate being crudely mixed into the other ingredients by stirring with a brass rod. In these and subsequent tests, which were conducted at S.P.& E.E., Shoeburyness, the blast produced by the bursts was measured by means of aluminium cantilever blast meters (2), and expressed in terms of equivalent weight of Plastic Explosive No. 3A. Particulars and results of these trials are shown in Tables 2 and 3.

TESTS ON 100 LB OF PROPELLANT IN 12-INCH DIAMETER CONTAINERS

TABLE 2

Series A, Heating Trials

Shot No.	Material	Type of Burst and Time Interval	Explosive Equivalent, lb of P.E., Determined from Blast Meters
A1	Ammonium perchlorate alone	Explosion after 13¼ min	Blastmeters destroyed by pieces of the container
A2	Polyester + Ionol + aluminium. Perchlorate added but unmixed	Mild explosion after 9¼ min	2.6
A3	As A2, but perchlorate crudely mixed in	Mild explosion after 4¼ min	3.4
A4	Fully mixed at E.R.D.E.	Mild explosion after 4 min	2.7

/TABLE 3 .....

TESTS ON 100 LB OF PROPELLANT IN 12-INCH DIAMETER CONTAINERS

TABLE 3

Series B, Trials with Igniters

Shot No.	Material	Type of Burst and Remarks	Explosive Equivalent, lb of P.E., Determined from Blastmeters
B1	Ammonium Perchlorate alone	Small amount of white smoke from igniter lead hole, followed by explosion after 2 - 3 s. Some perchlorate left on base plate	4.8
B2	Polyester + Ionol + Aluminium perchlorate added but unmixed	Explosion after a fraction of a second. Polyester but no perchlorate left on base plate	4.2
B3	Polyester + Ionol + aluminium. Perchlorate added and crudely mixed in	Similar to B2	4.9
B4	P2 propellant less T.D.I., fully mixed at E.R.D.E.	Immediate explosion, end plate blown off, propellant burned fiercely	4.6

No craters were formed in either the A or the B trials.

It was suspected that the blast registered, which showed only rather slight variations from shot to shot, might correspond to the bursting pressure of the vessels, and not to any explosive effect from the propellant. One of the containers was therefore burst by nitrogen pressure (at a pressure of 2500 p.s.i.), but the blast meters failed to register any appreciable deflection. It is considered possible, however, that the vessel might have burst at a higher pressure if it had been possible to apply nitrogen pressure as quickly as the pressure generated by the propellant. The result of the trial with nitrogen is therefore inconclusive.

Typical views of two of the containers are shown in Figs. 5 and 6. In Fig. 5 it will be seen that one end of the vessel came off prematurely, before the full bursting pressure of the tube was reached.

3.3 Tests on 1000 lb of Uncured Propellant in "Mock-up" Incorporators

From the 100 lb trials reported above, it appeared that the materials tested were capable of producing an explosive effect equivalent to about 5 per cent of their weight, but it was impossible to predict whether 1000 lb of propellant would behave similarly. Two mock-up incorporators, 3 ft diameter and 3 ft 6 inches high over the dished ends, made from ⅛-inch mild steel plate (Fig.7) were therefore half-filled with 1000 lb of uncured P2 propellant (less T.D.I. cross-linking agent). One was

/heated .....

heated over an Avtag fire until it burst, and the other was exploded by means of a 7-gram SR 371C igniter buried in the propellant, after heating for three days in a water tank at about 180°F (82°C) to simulate the mixing temperature. The temperature reached at the centre of the propellant was 60°C. The first vessel gave a very mild explosion with no measureable blast, while the second produced blast equivalent to only about 3 lb of P.E.

Since, in the earlier, small-scale, trials, no marked differences has been found between partially mixed and fully mixed propellants, the tests on the 1000 lb scale were done only on uncured propellant which had been fully mixed at E.R.D.E.

The remains of one of these incorporators after testing are shown in Fig 3.

3.4 Tests on Fully Cured Propellants in 12-inch Diameter Containers

Further trials were carried out, by agreement with the Director of Safety Services, to determine the behaviour of the propellants after filling into rocket motors, during curing and in subsequent storage.

Since it appeared from the results of previous trials that the 100 lb containers, 12 inches in diameter, produced conditions at least as stringent (as judged by the amount of blast produced) as the weaker 1000 lb containers, diameter 36 inches, it was agreed to use the 100 lb type, thus effecting a considerable economy in materials, In order to improve the consistency of the pressure at which the containers burst, the design was modified to prevent the ends blowing off (Fig.9), thus allowing the bursting pressure of the seamless tubing to be reached.

As well as the P2 propellant used for previous trials, propellant U 322 was included. This had a higher perchlorate content than P2 propellant, its composition being:

Ammonium perchlorate	74
Polyurethane rubber (Polyester + T.D.I.)	20
Aluminium	5
Ionol	1

A set of four containers was half-filled with each of the two propellants, and, for comparison, two containers were tested with ammonium perchlorate alone.

Since it was not appropriate to use an igniter within the charges, because in practice there would be no probable internal source of ignition corresponding to the stirrer during mixing, the containers were all heated over Avtag fires to simulate an accidental fire in a store or process building.

To simulate the temperature during curing, the containers and propellant were preheated to 60°C. This had not been done in the previous trials in which the containers were heated over Avtag fires, but it was thought to be desirable, because the heating time over a fire was usually so short that the temperature at the centre of the propellant when not preheated might not have risen appreciably above the air temperature.

/The .....

The results, with P.E. equivalents derived from the blastmeter readings, are given in Table 4. On this occasion the blastmeters were calibrated specially by firing a 5-lb P.E. charge at each of the two firing stations with the blast meters occupying the same positions as during the trials, so that these results may be regarded as somewhat more accurate than those previously quoted, which were based on calibrations made during an earlier study (2).

TABLE 4

Tests on 100 lb. of Propellant in 12-inch Diameter Containers of Stronger Design

Material	Quantity, lb	P.E. Equivalent; lb of P.E. No. 3A	Remarks
Ammonium Perchlorate	81.5	0.8	Pressure burst
" "	68	0.8	" "
Propellant P2	100	1.4	Very mild explosion
	"	1.6	"
	"	1.2	"
	"	1.0	"
Propellant U.322	100	1.7	"
	"	0.8	"
	"	3.1	"
	"	3.0	"

The strengthened containers all failed, as intended, in the seamless tubes, the ends remaining in position. The bursting strength had been calculated as 3160 p.s.i., the tensile strength of the tube material having been determined as 68,300 p.s.i. Flame was seen coming from a split in the side of several of the containers some considerable time before they blew up. Fig. 10 shows a typical view of one of these containers after test.

4. CONCLUSIONS

4.1 From a limited number of trials, it does not appear that there is a critical stage, during the mixing of the ammonium perchlorate with the other ingredients, when the polyurethane propellant is particularly susceptible to detonation. This aspect is being investigated further, in laboratory studies.

4.2 No marked difference in behaviour was found between uncured and cured propellant.

4.3 When ignited by external heating or by means of an igniter within the charges, the propellant showed no signs of detonating, and produced only a small amount of blast.

4.4 As a result of these trials, D.S.S. agreed that the propellants tested could be regarded as a "Y" risk when filled into rocket motors, and

/that .....

that "Y" safety distances could be used during processing, but with protection for the operatives against fragments.

4.5 The 12-inch diameter vessels containing 100 lb of propellant appeared to be quite suitable for use in future trials to simulate an incorporator containing 1000 lb of propellant, or a large-diameter rocket motor rendered non-propulsive by leaving the ends open.

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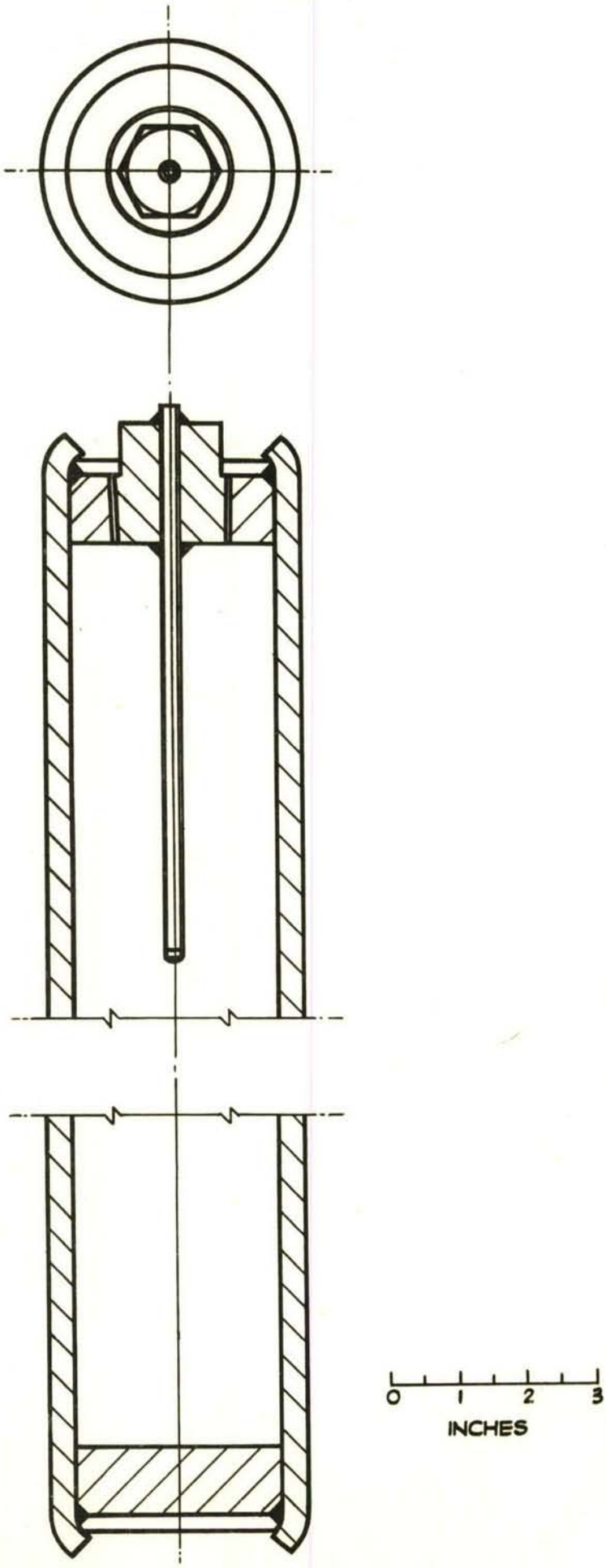
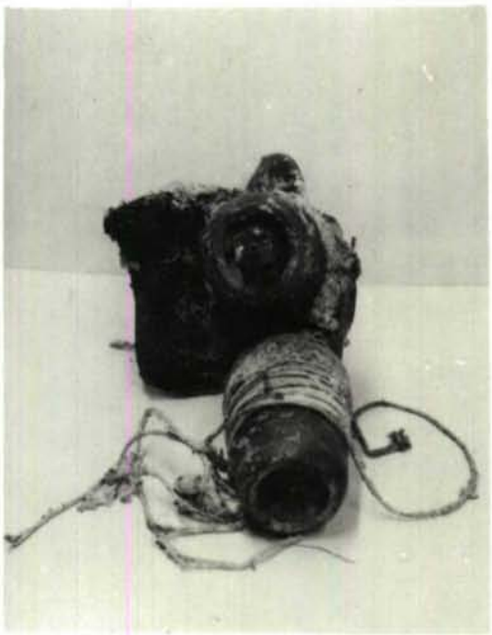


3 INCH I.D. THICK-WALLED VESSEL. FIG. 1.

SHOT No. 1. AMMONIUM PERCHLORATE ALONE.



SHOT No. 2. AMMONIUM PERCHLORATE UNMIXED WITH OTHER CONSTITUENTS.

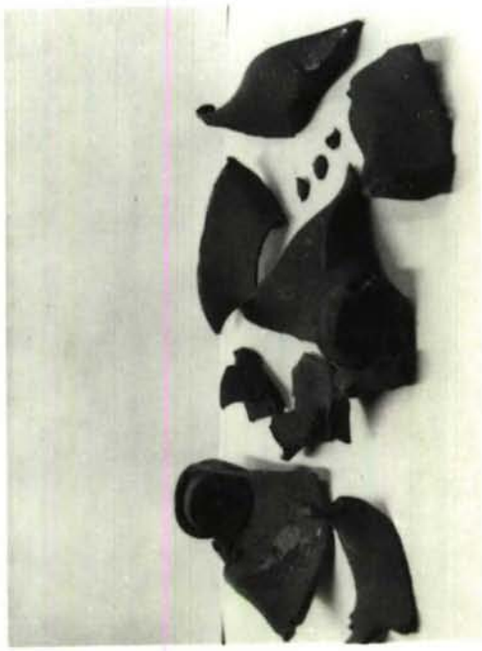
SHOT No. 3. AMMONIUM PERCHLORATE MIXED FOR 5 MINUTES WITH OTHER CONSTITUENTS.

SHOT No. 4. FULLY MIXED PROPELLANT

SHOTS 1, 2, 3 AND 4, CONTAINER EXTERNALLY HEATED ELECTRICALLY.

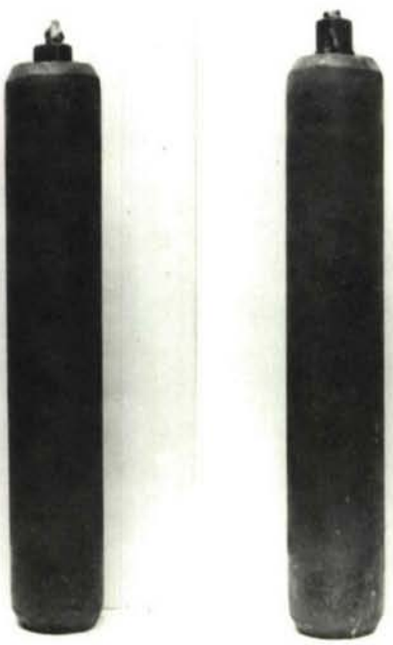
FIG. 2.

SHOT No. 5. AMMONIUM PERCHLORATE MIXED FOR 1 MINUTE WITH OTHER CONSTITUENTS



SHOT No. 6. FULLY MIXED PROPELLANT

SHOTS 5 AND 6. SR. 371 C. IGNITER AT CENTRE OF PREHEATED PROPELLANT.

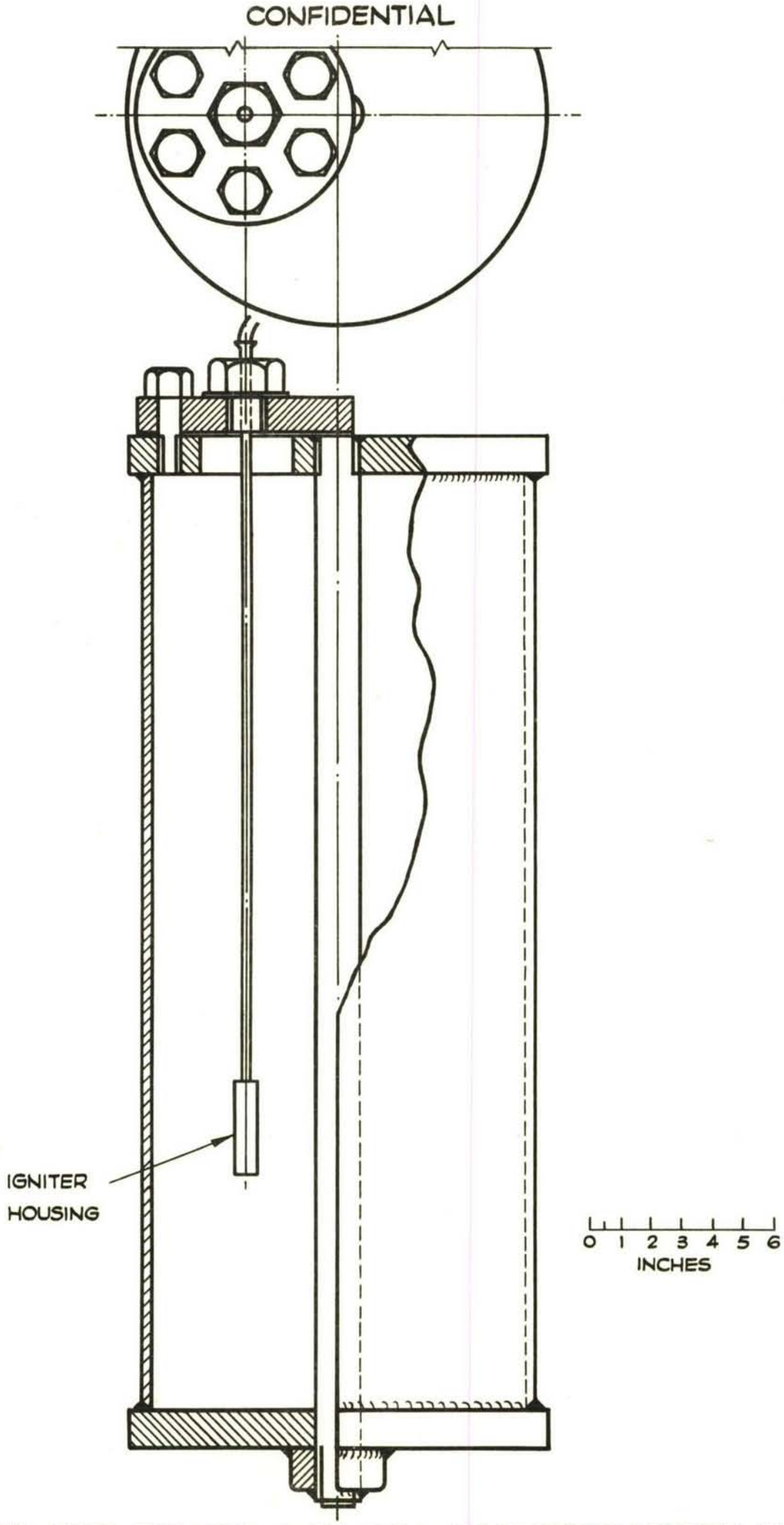


SHOT No. 8. SHOT No. 7.

SHOTS 7 AND 8. SR. 371. C. IGNITER ABOVE SURFACE OF PREHEATED PROPELLANT

SHOT No. 9. SHOT 9, S.R. 371 C. AT CENTRE OF PREHEATED PROPELLANT.

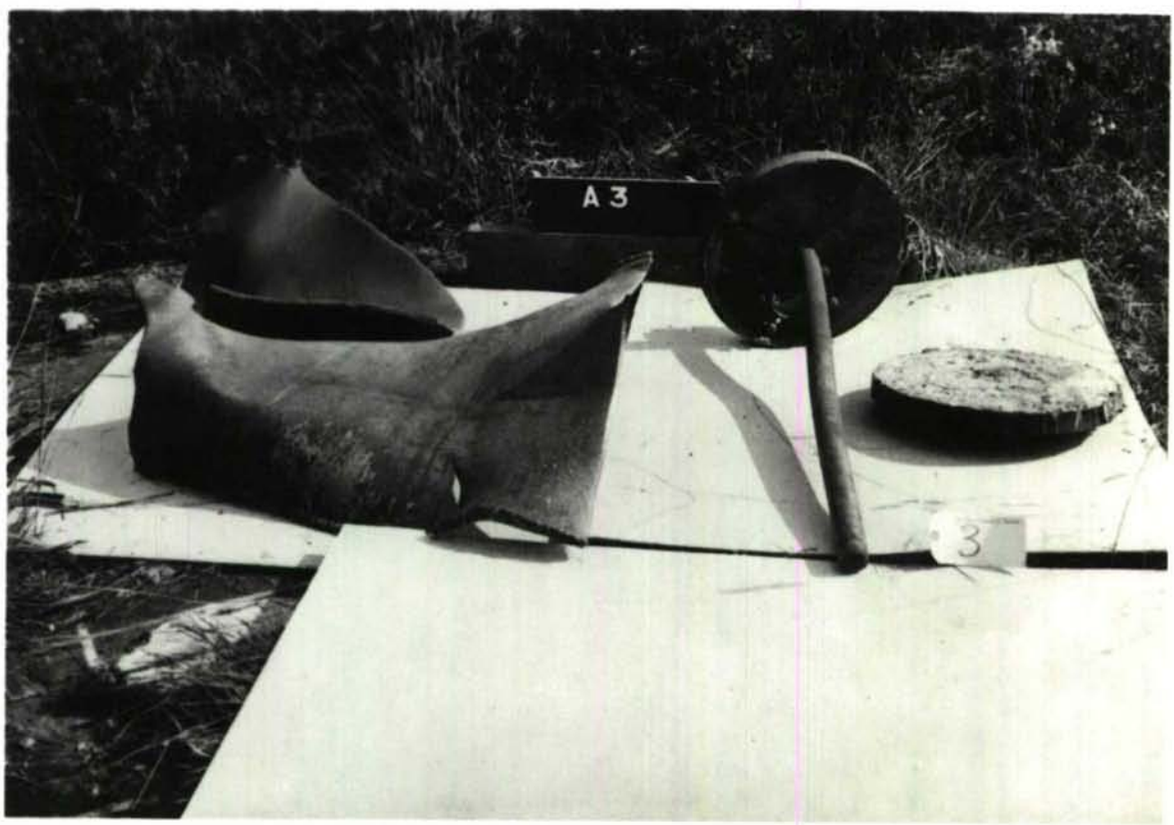
FIG. 3.



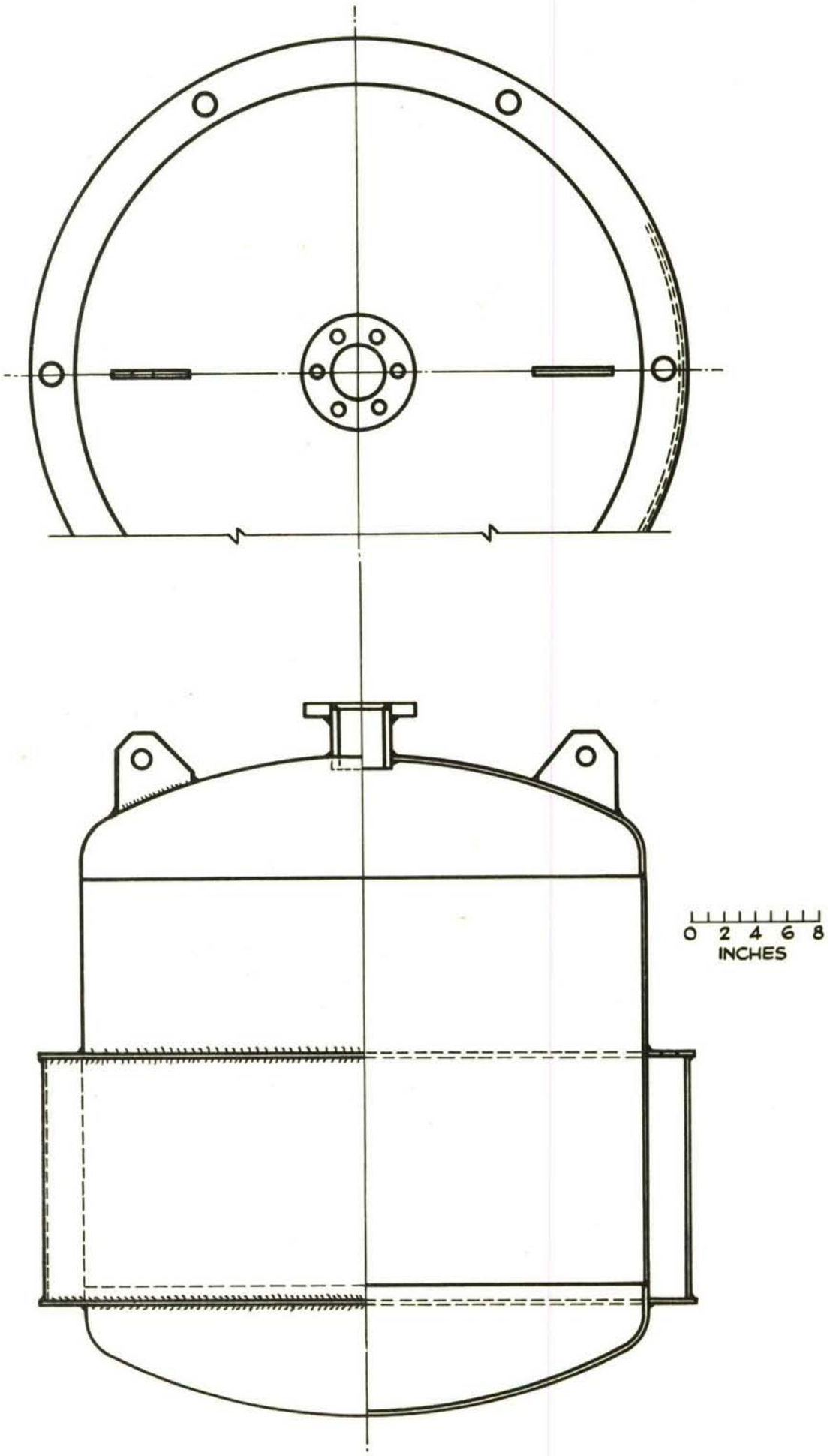
VESSEL USED FOR TRIALS ON 100 lb. OF UNCURED PROPELLANT.

FIG. 4.

TYPICAL VIEW OF "100 lb." VESSEL, THE END OF WHICH BLEW OFF BEFORE THE BURSTING STRENGTH OF THE TUBE WAS REACHED. CONSTRUCTION OF VESSEL AS SHOWN IN FIG. 4. USED WITH UNCURED PROPELLANT. FIG. 5.



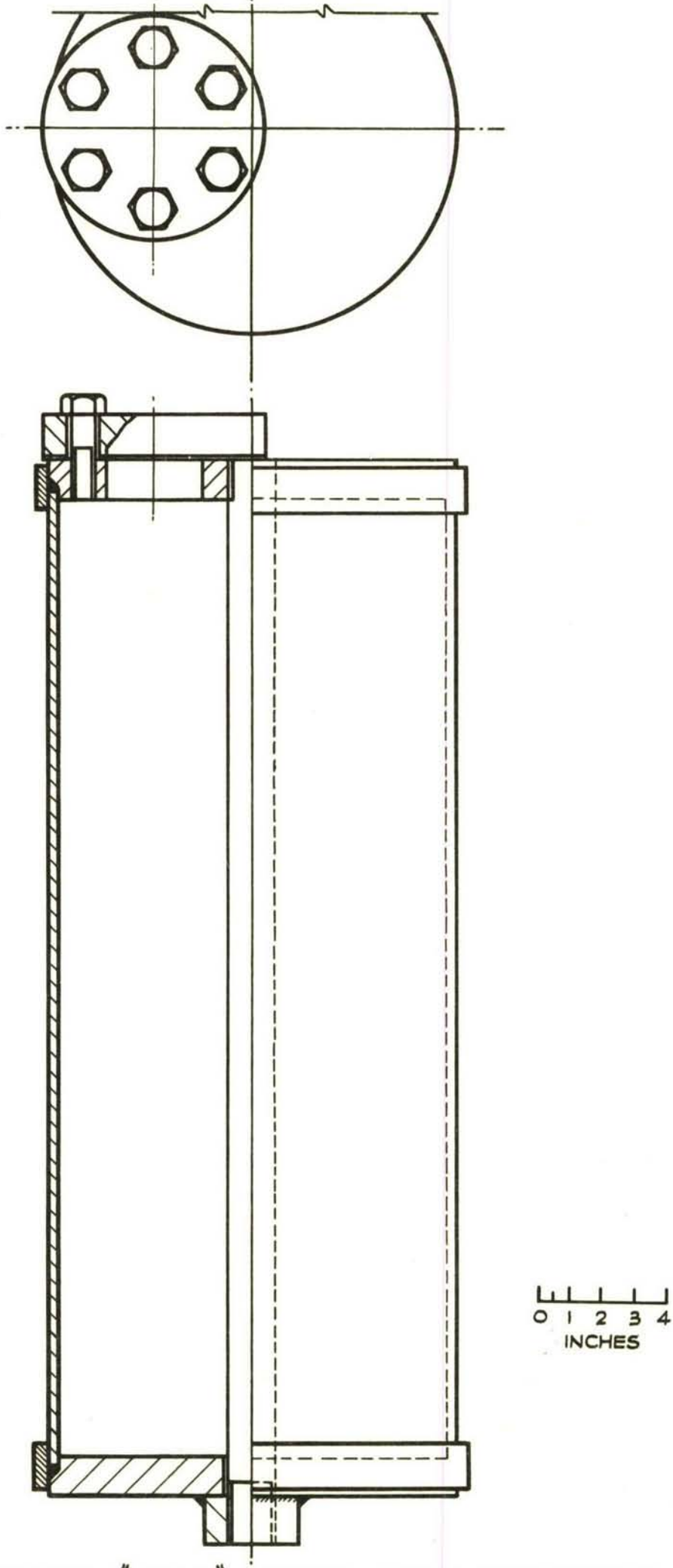
TYPICAL VIEW OF VESSEL AS IN FIGS. 4 AND 5, WHERE THE BURSTING PRESSURE OF THE TUBE WAS REACHED. FIG. 6.



MOCK-UP INCORPORATOR USED FOR TRIALS ON 1000 lb. OF UNCURED PROPELLANT. FIG.7.

MOCK-UP INCORPORATOR AFTER FIRING. FIG. 8.

TYPICAL VIEW OF STRENGTHENED "100 lb." VESSEL USED FOR TRIALS ON CURED PROPELLANTS. ALL BURSTS OCCURRED IN THE TUBES, NOT AT THE ENDS. FIG. 10.



STRENGTHENED "100 lb" VESSEL USED FOR TRIALS ON CURED PROPELLANT. FIG. 9.

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8 pp., 10 fig., 4 tables

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